react with acetyl chloride and acetic anhydride in the presence of one mole equivalent of pyridine (per mole of steroid) for three hours at reflux temperature, the majority of the starting material was recovered. When the reaction time was increased to 15 hours, the furostadiene diacetate II was obtained in 55% yield and if the heating period was further extended to 24 hours, II was isolated in a yield of 85%. The Schering workers[1] have reported that in the absence of pyridine the reaction proceeds in a period of 4 hours, but no yield of the reaction product is given. Nevertheless, the present results are in marked contrast to the ease of ring opening in the enol acetylation studies and suggest that the base itself is not the effective catalyst. Since in the latter reaction pyridine hydrochloride would be present in the mixture, the isomerization was attempted on 22-iso-5-spirosten-3β-ol (Ib) itself, and it was found that after 5 hours the furostadiene diacetate II could be obtained in 80% yield. That such an increased reactivity was due to the pyridine hydrochloride was demonstrated by allowing the acetate Ia to react with acetic anhydride and the salt for 5 hours, whereupon the diacetate II was isolated in a yield of 84%. Furthermore, the salt must be of a strong acid since the monoacetate Ia was obtained from the free alcohol Ib when only acetic anhydride and pyridine were employed.

It was found, however, that when the isospirostan was allowed to react with pyridine hydrochloride in a non-acetylating solvent such as methanol, only the starting material was recovered. Such a result emphasizes the fact that the formation of the 26-acetate is a necessary step in the isomerization reaction. This latter might be expected in view of the reported[1] reconversion of II to I under acidic hydrolysis conditions.

Experimental

Reaction of 22-Iso-5-spirosten-3β-ol Acetate (Ia) in Presence of Pyridine.—A mixture of 1.00 g. (2.1 mmoles) of the acetate (m.p. 188–190°), 5 ml. of acetic anhydride, 1 ml. of acetyl chloride (purified) and 0.168 g. (2.1 mmoles) of pyridine was heated under reflux for 3 hours, cooled to 50° and the solvents removed under reduced pressure. The dark red solid residue was dissolved in hot methanol, treated with Norit and the solution deposited 0.87 g. of white crystals, m.p. 170–177°. Recrystallization yielded 0.68 g., m.p. 187–189°. Concentration of the mother liquors yielded only a small amount of crystalline material which upon further recrystallization melts from 140–145°.

When the reaction was allowed to reflux for 15 hours and processed as above, the solid from the first methanol recrystallization amounted to 0.56 g., m.p. 87–91°, and the mother liquor upon standing deposited a further quantity of similar material. The total solid was recrystallized from ethanol (Norit); yield 0.59 g. (55%), m.p. 95–98°, $[\alpha]^{25}\mathrm{D}$ −48.8° ($CHCl_3$). Gould, Staeudle and Hershberg[1] report m.p. 93–98° for their crude material from the aluminum chloride catalyzed isomerization and m.p. 98.5–100.5°, $[\alpha]^{25}\mathrm{D}$ −47.0° ($CHCl_3$), after chromatography.

When 2.0 g. of the acetate Ia was allowed to react with 10 ml. of acetic anhydride, 2 ml. of acetyl chloride and 0.336 g. of pyridine for 24 hours and processed as above, 1.83 g. (85%) of the diacetate was obtained, m.p. 94–97°, $[\alpha]^{25}\mathrm{D}$ −47.2° ($CHCl_3$). The infrared spectrum was identical with that prepared by the aluminum chloride method.

Reaction of 22-Iso-5-spirosten-3β-ol (Ib) in Presence of Pyridine.—A mixture of 2.0 g. (4.7 mmoles) of the alcohol Ib, m.p. 204–206°, 10 ml. of acetic anhydride, 2 ml. of acetyl chloride and 0.37 g. (4.7 mmoles) of pyridine was heated under reflux for 5 hours, the reaction mixture concentrated under reduced pressure and the residue dissolved in 50 ml. of methanol. After concentration to 25 ml. and cooling, 1.2 g., m.p. 92–95°, of solid was obtained and further concentration of the mother liquor yielded an additional 0.9 g. The combined materials were recrystallized from 20 ml. of methanol; yield 1.86 g. (80%), m.p. 95–98°, $[\alpha]^{21}\mathrm{D}$ −47.8° ($CHCl_3$).

Reaction of 22-Iso-5-spirosten-3β-ol Acetate in Presence of Pyridine Hydrochloride.—A mixture of 2.0 g. of the acetate, 10 ml. of acetic anhydride and 0.65 g. of dry pyridine hydrochloride was heated for 5 hours and processed by pouring into ice-water. After filtration and recrystallization, the diacetate II was identical with the above; yield 1.8 g. (84%).

Acknowledgment.—The authors are indebted to Merck and Co., Inc., for generously supplying the diosgenin acetate.

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The Reaction of Diphenyliodonium Ion with Hydroxide Ion[1]

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RECEIVED MARCH 27, 1954

The decomposition of diaryliodonium salts has been represented both as an ordinary nucleophilic displacement on the aromatic system by the anion,[2] and as a unimolecular decomposition to give an aryl cation and the aryl iodide.[3] Qualitative evidence on the direction of fission of unsymmetrical iodonium salts[4,2a] and on the stabilities of salts with anions of different nucleophilic power[5] both suggested that the unimolecular mechanism was unlikely in that the results of both are predictable on the basis of an analogy to the bimolecular displacement of chlorine from substituted chlorobenzenes.[2b] This evidence does not rigorously exclude the unimolecular mechanism, however, since the systems were in most cases heterogeneous. Because of our interest in aryl cations derived from diazonium salts, we have searched for other sources of these ions, and had investigated the hydrolysis of iodonium salts from this viewpoint, before the appearance of the further evidence of Beringer and co-workers[2a] which made the unimolecular mechanism very improbable.

Not only is the order not definitely established but the products are complicated by the possibility of consecutive reactions. By the bimolecular path the reactions would be 1 and 2

$$(C_6H_5)_2I^+ + OH^- \longrightarrow C_6H_5I + C_6H_5OH \quad (1)$$

$$(C_6H_5)_2I^+ + OC_6H_5^- \longrightarrow C_6H_5I + (C_6H_5)_2O \quad (2)$$

Diphenyl ether has indeed been detected by Beringer,[2a] but since it might also arise from the phenyl cation, the unimolecular reaction cannot be eliminated on this basis.

Kinetic measurements of even a crude sort will tell whether or not the rate of decomposition of diphenyliodonium ion is dependent on the hydrox-

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[1] From the M.A. Thesis of C. A. Stout, 1953.

[2] (a) F. M. Beringer, A. Brierly, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2708 (1953); (b) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

[3] H. J. Lucas, E. R. Kennedy and C. A. Wilmot, THIS JOURNAL, **58**, 157 (1936).

[4] R. B. Sandin, M. Kulka and R. McCready, *ibid.*, **59**, 2014 (1937).

[5] R. B. Sandin, F. T. McClure and F. Irwin, *ibid.*, **61**, 2944 (1939).

ide ion concentration, but very refined data would be necessary to confirm a sequence such as 1 and 2, because of the well known complications of such systems. We have attempted only the first objective and have found that the rate depends on the hydroxide ion concentration. With a large excess of sodium hydroxide in water solution the disappearance of diphenyliodonium chloride followed a first order course as far as it was followed (not more than 60% completion). However, the resulting pseudo first order rate constants were proportional to the hydroxide ion concentration as shown in Fig. 1. The second order rate constant derived from these data is 7.3×10^{-5} l./mole/sec. at 59.1°. Since the latter part of the reaction when most of the diphenyl ether formation presumably occurred was not observed, the complication of consecutive reactions was small. These results unequivocally eliminate the first-order carbonium ion mechanism and they are not inconsistent with the sequence 1 and 2. They are not accurate enough to give strong support to the above mechanism, however. Complications due to inhomogeneity are discussed later.

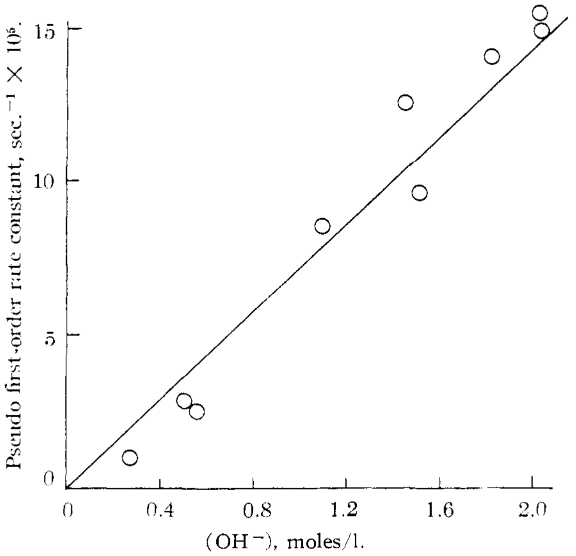

Fig. 1.—Effect of hydroxide ion concentration on the rate of decomposition of diphenyliodonium chloride.

The reaction sequence proposed is convenient in that the kinetically complicated consecutive second-order reactions can be experimentally reduced to two competitive pseudo first-order reactions by using large excesses of both hydroxide and phenoxide ions. When this is done the differential equation showing the relative rates of formation of phenol and diphenyl ether can be readily integrated to give 3

$$\frac{((C_6H_5)_2O)}{(C_6H_5OH)} = \frac{k_2}{k_1}\frac{(OC_6H_5^-)_0}{(OH^-)_0} \qquad (3)$$

where the concentrations on the left show those of the products at any time, in particular the end, those on the right the initial and virtually constant concentrations of the two reagents.

The yields were determined by a rather crude bromometric analysis for diphenyl ether and the yields of this substance under various conditions are shown in Table I. By estimating the phenol yield by difference the ratio k_2/k_1 has been calculated from these data in the last column. The values in brackets are those obtained under conditions different from those required for accurate application of equation 3. The hydroxide ion in these cases is estimated from the hydrolysis of phenoxide ion. The phenoxide ion is a rough average value equal to one half the initial iodonium salt concentration.

TABLE I

YIELDS OF DIPHENYL ETHER FROM DIPHENYLIODONIUM CHLORIDE, SODIUM HYDROXIDE AND SODIUM PHENOXIDE

(OH^-)	$(OC_6H_5^-)_0$	$(C_6H_5)_2O$, %	k_2/k_1
[3×10^{-3}]	0.1	30	[1.3×10^{-2}]
[3×10^{-3}]	.2	67	[3.2×10^{-2}]
[3×10^{-3}]	.5	100	
1.0	[.01]	24[a]	[30]
2.02	[.02]	18[b]	[20]
1.84	.2	22	2.6
1.54	.5	30	1.3
1.45	.5	30	1.2
0.6	.5	26	0.42
.95	1.0	38	.58
.45	0.5	35	.60
.30	0.65	48	.43

[a] Phenol yield 70%. [b] Phenol yield 80%.

It is immediately obvious that the last column is not nearly constant, even if the somewhat uncertain values in brackets are not heavily weighted. While the analytical precision is not high, the error would have to be enormously greater than is suggested by the sample analyses and those cases where phenol was also determined to make the column constant. The data thus lead to the conclusion that equation 3 is incorrect and that reactions 1 and 2 are insufficient or incorrect.

A possible objection to this argument is the fact that the solutions become heterogeneous due to the formation of iodobenzene, and that the rates are sensitive to the presence of the second phase. Such a sensitivity can be ascribed only to a partition of some reagent between the two phases, but since all reagents in reactions 1 and 2 are ions this would not be expected. Of course some other mechanism involving a neutral molecule might well be sensitive to the appearance of a second phase. However, the data on yields are invalid only if the conclusion drawn from them is correct.

The rather unexpected conclusion that neither a simple unimolecular reaction nor the straightforward sequence of bimolecular reactions is adequate has received independent confirmation. It was observed that the mixtures frequently became yellow during a run although the final products were colorless. A further investigation at room temperature led to the observation that certain solutions of sodium hydroxide, diphenyliodonium chloride and phenol precipitated a yellow oil, soluble in hydroxide to give a yellow solution and in acid to give a colorless solution. These reactions were reversible and did not consume the iodonium ion. Since this oil was heavily contaminated with phenol, it was not analyzed.

The presence of this compound of undetermined structure in this solution shows that diphenyliodonium ion can undergo some reversible reaction with the reagents present in the other runs, and therefore the reaction must be more complicated than reactions 1 and 2 alone would indicate, in complete accord with the results deduced from the yield measurements.

Experimental

Materials.—Diphenyliodonium iodate was made essentially by the method of Lucas and Kennedy.[6] The chloride was made from this by precipitation from solution with sodium chloride and recrystallization from alcohol. *Anal.* Calcd. for $C_{12}H_{10}ICl$: Cl, 11.2. Found: Cl, 11.2 (by titration with mercuric nitrate).

Rate Measurements.—An appropriate solution of sodium hydroxide, sometimes containing sodium nitrate to adjust the ionic strength, was heated in a thermostat to 59.1 ± 0.04° and solid diphenyliodonium chloride was then dissolved in this as rapidly as possible. Samples were then taken at various times and analyzed for iodonium ion. This analysis consisted in pipetting the sample into a cold solution of sodium iodide, filtering the resulting diphenyliodonium iodide on a weighed filtering crucible, washing with water and ether, then drying in a vacuum desiccator and weighing. On known solutions of concentrations within the range used this analysis was about 2% low. Solutions of the iodonium chloride were apparently stable in the absence of hydroxide ion, and in the presence of 0.1 *N* bromide ion no perceptible reaction (less than 10%) occurred in 40 hr. at 100°.

Product Analysis.—Phenol was determined by bromination in reaction mixtures in which no phenol or sodium phenoxide was used as a starting material. Diphenyl ether was estimated by a bromination method after separation from phenol by repeated partition of the reaction mixture between carbon tetrachloride and aqueous sodium hydroxide followed by removal of most of the solvent. At room temperature in two hours diphenyl ether in a small amount of carbon tetrachloride reacted with 1.00 ± 0.05 mole of bromine derived from an acidified standard solution of sodium bromate and sodium bromide. The excess bromine was determined iodometrically. The product of this reaction is presumably mostly *p*-bromodiphenyl ether,[7] but it was not isolated. The accuracy of this analysis is not high; an indication of the accuracy can be obtained from the two runs where phenol was also determined, in these cases phenol and diphenyl ether together accounted for 94 and 98% of the total reaction product.

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[6] H. J. Lucas and E. R. Kennedy, *Org. Syntheses*, **22**, 52 (1942).

[7] A. Mailhe and M. Murat, *Compt. rend.*, **154**, 601 (1912); C. M. Suter, This Journal, **51**, 2381 (1929).

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The Anomalous Carbonylation of Diphenylacetylene[1]

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RECEIVED MAY 1, 1954

Shortly after descriptive reports of carbonylation of olefins and acetylenes became available[3,4] we became interested in predicting the direction of addition of hydrogen and carboxyl to the unsaturated center. Since the other groups in substituted ethylenes and acetylenes would be most likely to influence both the rate and direction of carbonylation, a number of symmetrical and unsymmetrical acetylenes were chosen for study. The work was prematurely interrupted and results of more extensive investigations of this kind have since been published.[5] Our experience with ethyl tetrolate, phenylacetylene and diphenylacetylene is in accord with the results and predictions of the British group. Although our reaction medium was not the same as that employed in the standard conditions adopted by them,[5a] we also noted that certain carbonylations proceeded slowly with no temperature rise while others were exothermic. The latter were always accompanied by a deep blood-red color changing instantly to the pale green of the nickel solution with exhaustion of either the acetylene or the nickel carbonyl. In addition we wish to report the curious behavior of diphenylacetylene on carbonylation in dioxane medium.

The non-availability of detailed experimental procedures at the inception of this work necessitated casting about for suitable conditions in each case. Diphenylacetylene in ethanol and benzene gave the expected ethyl α-phenylcinnamate in 34% yield, some starting material being recovered. When dioxane and ethanol were used as solvents, this ester was also produced, but the principal reaction product was a white, granular material, which after recrystallization melted at 161–162°. This compound was neutral and unsaponifiable, permanganate and bromine tests for unsaturation were negative, and no carbonyl derivative could be obtained in spite of determined efforts to prepare an oxime, phenylhydrazone or 2,4-dinitrophenylhydrazone. The infrared spectrum in Nujol was prepared and interpreted through the courtesy of Dr. H. S. Gutowsky of the University of Illinois, who suggested the presence of a carbonyl group, a double bond possibly conjugated with the former, and one or more phenyl groups.

The compound proved to be 2,3,4,5-tetraphenylcyclopenta-2-en-1-one which, though previously known, was not suspected in this case because our analytical results gave consistently low carbon values. The identity was noted from a comparison of physical data and the review of chemical reactivity of this compound given by Sonntag, *et al.*[6] Our product seemed to be the same in all respects, chemical properties, ultraviolet and infrared absorption, except for the carbonyl absorption reported at 5.85 μ. We had found this band at 5.91 μ. An authentic sample was supplied through the courtesy of Dr. Becker. This was identical in physical appearance, melting point and mixed melting point. The infrared curves of both compounds obtained using potassium bromide discs[7] were superimposable and showed the carbonyl absorption at 5.92 μ.

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[1] Part of this work is abstracted from the thesis submitted by Frank L. MacArtor to the faculty of the University of Tennessee in partial fulfillment of requirements for the M.S. degree in chemistry.

[2] G. D. Searle and Co., Skokie, Ill.

[3] "A New Synthesis of Acrylic Acid," J. W. Reppe, (translation by I. G. Callomon and G. M. Kline), *Modern Plastics*, **23**, 162 (1945).

[4] C. Schuster and A. Simon, U. S. Department of Commerce, Office of Technical Service, PB No. L70326 (2) (April 23, 1940) (see "Bibliography of Scientific and Industrial Reports," Vol. 8, No. 1, July 4, 1948, p. 6).

[5] (a) E. R. H. Jones, T. Y. Shen and M. C. Whiting, *J. Chem. Soc.*, 230 (1950); (b) *ibid.*, 48 (1951); (c) *ibid.*, 763 (1951).

[6] N. O. Sonntag, S. Linder, E. I. Becker and P. E. Spoerri, This Journal, **75**, 2283 (1953).

[7] We wish to thank Dr. R. T. Dillon, G. D. Searle and Co., for these determinations.